Journal of Organometallic Chemistry, 386 (1990) 195–201
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20618

The use of $[Fe(CO)_3NO]^-$ for the carbonylation of primary, secondary and allylic halides

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(Received October 23rd, 1989)

Abstract

The tricarbonyl nitrosyl ferrate anion (**1**) is an efficient carbonylation reagent for the formation of methyl esters from primary and secondary alkyl and benzyl halides. The carbonylation of allyl halides results in the exclusive formation of β,γ-unsaturated esters. Studies of the catalytic use of **1** are also described.

Introduction

Whilst the hydroformylation of alkenes is one of the most widely used organometallic processes for the formation of carbon–carbon bonds it suffers from a lack of complete regiospecificity. Generally linear aldehydes are the major products from this reaction [1], although recent reports [2,3] have shown that in certain cases the reaction can be controlled to give the branched aldehydes selectively.

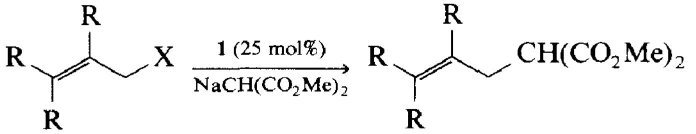
An attractive alternative to the hydroformylation reaction is direct carbonylation of regiospecifically prepared primary and secondary alkyl halides (eq. 1). The palladium-catalysed carbonylation of aryl halides is a well established process [4], but the carbonylation of allyl halides generally requires high temperatures and high carbon monoxide pressures [5], and even under milder conditions mixtures of α,β- and β,γ-unsaturated esters are obtained [6]. Alkyl halides generally undergo β-hydrogen elimination in preference to palladium-catalysed carbonylation. Reactions based on nickel [7] and cobalt [8] carbonyl complexes have been studied, but very little work has been carried out with systems based on the inexpensive iron pentacarbonyl.

$$RX \xrightarrow[\text{[M]}]{\text{CO, R'OH}} RCO_2R' \qquad (1)$$

0022-328X/90/$03.50

Iron pentacarbonyl itself has been shown to be a moderately efficient catalyst for the carbonylation of benzylic halides but it shows very little reactivity towards other halo compounds [9]. Collman's reagent, $Na_2[Fe(CO)_4]$, can be used in the carbonylation of a variety of halo compounds via a two step process involving the oxidation of iron acyl complexes [10], but this reagent, is spontaneously inflammable, which makes routine use difficult [11]. Other iron-based systems have met with limited success [12].

The monoanion tricarbonylnitrosyl ferrate, $[Fe(CO)_3NO]^-$ (**1**), has been successfully used in the alkylation of allylic halides [13] and acetates [14] (eq. 2), and a recent patent describes its use in the preparation of esters of phenylacetic acid from benzyl halides [15] (eq. 3), although in both cases catalyst turnovers were low. We now report the use of $[Fe(CO)_3NO]^-$ as a reagent for the carbonylation of benzyl, allyl, and alkyl halides.



(2)

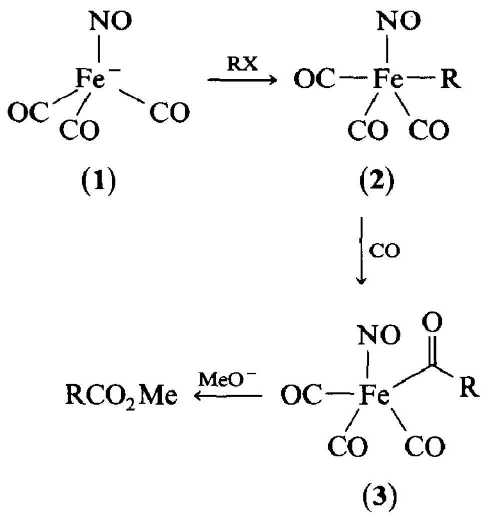
$$PhCH_2Br \xrightarrow[55\,^{\circ}C,\ 1.7\ bar\ CO]{1,\ NaOMe/MeOH} PhCH_2CO_2Me \qquad (3)$$

Results and discussion

Sodium tricarbonylnitrosyl ferrate is prepared from iron pentacarbonyl, sodium methoxide, and sodium nitrite [16]. **Extreme caution** should be exercised when preparing and handling this compound as it is very air-sensitive and has been found to decompose explosively. The tetrabutylammonium salt [13,17] is much easier to prepare and is moderately air stable, reducing the need for weighing and other manipulations to be performed under an inert atmosphere. The following studies were all undertaken with the tetrabutylammonium salt, but comparative studies involving the sodium salt showed no appreciable differences in reactivity between the two complexes.

Chaudhari et al. [18] have reported that reaction of alkyl halides with **1** gives alkyliron complexes (**2**), which are converted into acyliron complexes (**3**) in the presence of carbon monoxide (Scheme 1). Addition of a methoxide source to this reaction should therefore result in the formation of methyl esters. In the present study potassium carbonate and methanol were chosen as the source of methoxide to reduce the probability that nucleophillic attack would occur prior to carbonyl insertion, thereby giving the ether in preference to the ester. No change in yield was observed when sodium methoxide was used, but some of the corresponding ether (ROMe) was formed.

The results obtained from the carbonylation of various benzyl halides are summarised in Table 1. Both benzyl bromide and chloride are readily carbonylated to give the methyl ester by use of stoicheiometric amounts of **1** (reactions 1 and 2). Triphenylphosphine can be used in place of carbon monoxide, thus eliminating the need to perform the reaction in a pressure vessel (reaction 3). Preparation of the iron reagent in situ from tetrabutylammonium nitrite and iron pentacarbonyl also results in the carbonylation of benzyl bromide in high yield (reaction 4).



Scheme 1

Secondary benzyl halides are harder to carbonylate as they are often prone to β-hydrogen elimination when bound to metal complexes. Carbonylation of PhCH(Me)Br gave a moderate yield of ester along with a significant quantity of styrene. Reaction of the corresponding chloro compound gave a low yield of the ester along with recovered starting material. The absence of styrene in this latter reaction suggests that thermal elimination of HBr from the benzyl bromide rather than β-hydrogen elimination from an intermediate iron complex may be the origin of the styrene formed in the reaction of the bromo compound.

The carbonylation of heptyl iodide (**4**) with the iron reagent **1** gave a mixture of methyl octanoate (**5**) and octanal (**6**) in 63% overall yield (eq. 4). The ratio of ester to aldehyde varied from 2/1 to 3/1 but in all cases the ester was the major product. No starting material was recovered from the reaction, and heptane and 1-heptene were identified as the other products by GLC analysis of the reaction mixture. The

Table 1

Carbonylation of benzyl halides.

$$\mathrm{RX} \xrightarrow[50\,^{\circ}\mathrm{C},\ 15\ \mathrm{h}]{\mathbf{1},\ \mathrm{CO},\ \mathrm{K_2CO_3},\ \mathrm{MeOH}} \mathrm{RCO_2Me}$$

Reaction	RX	RCO_2Me yield (%)
1	$PhCH_2Br$	86
2	$PhCH_2Cl$	85
3	$PhCH_2Br$ [a]	86
4	$PhCH_2Br$ [b]	87
5	PhCH(Me)Br	48
6	PhCH(Me)Cl	22

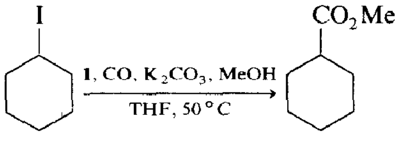
[a] Triphenylphosphine used in place of carbon monoxide. [b] $[Fe(CO)_3NO]^-$ prepared in situ from Bu_4NNO_2 and $Fe(CO)_5$.

formation of the products can be rationalised in the following way: β-hydrogen elimination from an alkyliron intermediate **2** gives heptene and an iron hydride species, which then transfers hydride to other alkyliron (**2**) and acyliron (**3**) complexes to form the heptane and octanal respectively.

$$\underset{(\mathbf{4})}{C_7H_{15}I} \xrightarrow[\text{THF, 50 °C, 15 h}]{\mathbf{1}\text{, CO, }K_2CO_3\text{, MeOH}} \underset{(\mathbf{5})}{C_7H_{15}CO_2Me} + \underset{(\mathbf{6})}{C_7H_{15}CHO} \qquad (4)$$

Reaction of heptyl bromide or the mesylate or tosylate derived from heptanol under identical conditions failed to yield any ester and starting material was recovered. The mesylate and tosylate could be carbonylated in low yield (35–40%) when a stoicheiometric quantity of tetrabutylammonium iodide was added to the reaction mixture; the mesylate or tosylate is presumably converted in situ into the iodide, which is then carbonylated.

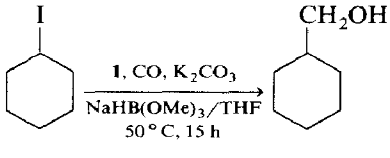
Reaction of cyclohexyl iodide (**7**) under the carbonylation conditions gave a good yield (80%) of the corresponding methyl ester (**8**) after 15 h and a virtually quantitative yield (93%) after 24 h (eq. 5). Only very small quantities (< 1%) of the aldehyde could be detected, which suggests that in the reaction of secondary halides insertion of carbon monoxide to form the acyl complex **3** is faster than the β-hydrogen elimination. Again the corresponding bromo compound failed to react, and starting material was recovered.



(5)

(**7**) (**8**)

When the reaction of cyclohexyl iodide **7** was carried out in the presence of a large excess of NaHB(OMe)$_3$, in place of the methanol and potassium carbonate, the primary alcohol **9** was formed in high yield (73%) (eq. 6). The reaction presumably proceeds via the formation of the aldehyde, which is then reduced to the alcohol. Reducing the amount of hydride present to less than one equivalent leads to a mixture of starting material and alcohol and not the aldehyde. Use of sodium borohydride as the hydride source gave only a poor yield (36%) of the alcohol along with the starting iodide.



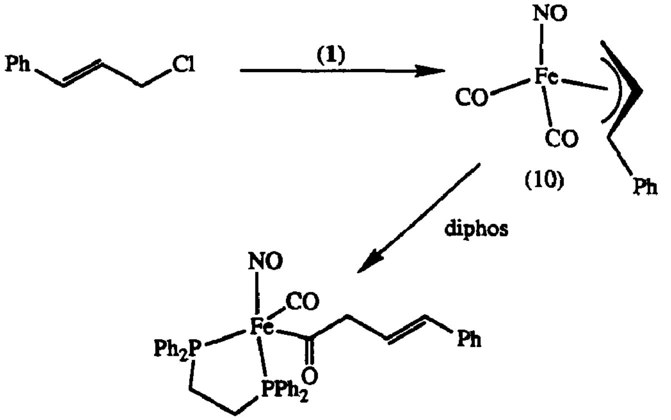
(6)

(**7**) (**9**)

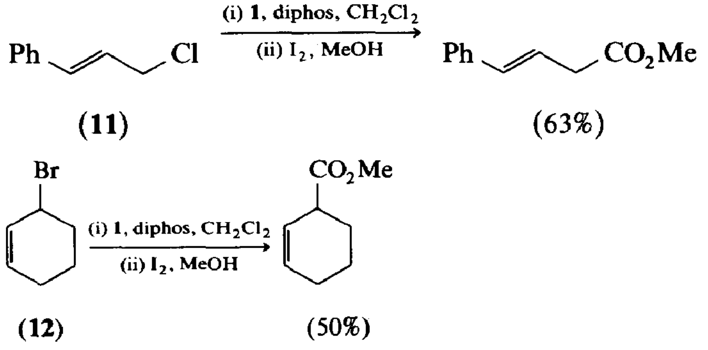
The carbonylation of allyl halides offers an attractive route to β,γ-unsaturated esters. The preparation of compounds of this type is not a trivial problem since under most reaction conditions the double bond moves into conjugation to form the α,β-unsaturated ester. The nickel catalysed carbonylation of allyl halides forms a mixture of the β,γ- and α,β-unsaturated esters in good yield [19]. Recently the palladium catalysed carbonylation of allyl ethers has been reported to produce

β,γ-unsaturated esters in high yield, although high temperatures and carbon monoxide pressures are required (100 °C, 30 atm CO) [20].

Allyl halides have been shown to react with **1** to form η^3-allyl dicarbonylnitrosyliron complexes (**10**) and insertion of carbon monoxide can be accomplished by the addition of diphos to the isolated complexes [21] (eq. 7).



Attempts to form methyl esters from allyl halides in a similar fashion to that described for alkyl iodides were not successful because the methanol adds to the intermediate allyliron complexes (**10**) to form the corresponding ethers. Carbonylation of the allyl halides can however, be achieved by use of a two step reaction sequence. The acyliron complex is first formed in a reaction of diphos and the allyl halide with **1**, and subsequent addition of methanol and iodine to the mixture gives the required ester. Reaction of cinnamyl chloride (**11**) and 2-bromocyclohexene (**12**) in this fashion gave acceptable yields of the β,γ-unsaturated methyl esters (eq. 8). No trace of the α,β-unsaturated compounds could be detected, although small amounts of the methyl ethers were present.



(8)

The use of **1** in catalytic amount was also investigated and the results are summarised in Table 2. The number of catalyst turnovers was determined by comparing the amount of carbonylated product to the amount of **1** added. The carbonylation of benzyl bromide involved a maximum of five turnovers after 6 h at 50 °C. Increasing the reaction temperature, reaction time, or carbon monoxide pressure did not increase the amount of carbonylated product.

Replacement of the methanol with diisopropylamine gave the corresponding amide with about 2 turnovers of catalyst, whilst use of diethylamine gave *N*,*N*-diethylbenzylamine.

Table 2

Catalytic carbonylation of alkyl halides

$$\mathrm{RX} \xrightarrow[50\,^{\circ}\mathrm{C},\ 15\ \mathrm{h}]{\mathbf{1},\ \mathrm{CO},\ \mathrm{K_2CO_3},\ \mathrm{MeOH}} \mathrm{RCO_2Me}$$

Reaction	RX	Conditions	Turnovers
7	$PhCH_2Br$	20 °C/6 h	5
8	$PhCH_2Br$ [a]	20 °C/15 h	2
9	$PhCH_2Br$ [b]	20 °C/15 h	0
10	MeI	20 °C/6–15 h	4–6
11	BuI	50 °C/6 h	2

[a] $^iPr_2NH$ used in place of MeOH. [b] Et_2NH used instead of MeOH formed *N*,*N*-diethylbenzylamine.

Methyl iodide was converted into methyl acetate with about 4–6 turnovers of catalyst after 15 h at room temperature. Carbonylation of butyl iodide resulted in only 2 turnovers of the catalyst after 15 h at 50 °C.

Conclusion

We have demonstrated that the carbonylation of a variety of primary and secondary alkyl halides can be effected by use of tetrabutylammonium tricarbonylnitrosyl ferrate. In the case of allyl halides the regiospecific formation of β,γ-unsaturated esters is observed. Work to determine the stereochemical outcome of the carbonylation of homochiral alkyl iodides is in progress.

Experimental

General. Tetrabutylammonium tricarbonyl ferrate was prepared as previously described [13]. The products from the carbonylation reactions were characterised by comparison with authentic samples.

General carbonylation procedure. Into a glass pressure vessel were placed tetrabutylammonium tricarbonylnitrosyl ferrate (**1**) (5 mmol except for results in Table 2 when 0.5 mmol was used), K_2CO_3 (15 mmol), the halide (5 mmol), methanol (1 ml) and THF (5 ml). The vessel was then pressurised with 4 atm of carbon monoxide. After 15 h stirring at 50 °C the mixture was filtered and the precipitate washed with dichloromethane.

Carbonylation of benzyl bromide using triphenylphosphine. A mixture of benzyl bromide (5 mmol), **1** (5 mmol), triphenylphosphine (5 mmol), K_2CO_3 (10 mmol), methanol (1 ml) and dichloromethane (5 ml) was stirred at 20 °C for 15 h. Diethyl ether was added to precipitate the iron residues, filtration and distillation then gave the ester in 86% yield.

Carbonylation of benzyl bromide using $Fe(CO)_5$. A mixture of $Fe(CO)_5$ (5 mmol), tetrabutylammonium nitrite (5 mmol), K_2CO_3 (10 mmol), and dichloromethane (5 ml) was stirred at 20 °C for 2 h. Methanol (1 ml) and benzyl bromide (5 mmol) were then added, the vessel was pressurised with 4 atm of carbon monoxide, and the mixture was stirred at 20 °C for 15 h. Filtration and distillation gave the ester in 87% yield.

Carbonylation of cyclohexyl iodide in the presence of $NaBH(OMe)_3$. A 1 *M* solution of $NaBH(OMe)_3$ (6 mmol) in THF was added to a mixture of (**1**) (2 mmol) and cyclohexyl iodide (2 mmol), the vessel was pressurised with carbon monoxide, and the mixture heated at 50 °C for 24 h. Dilute hydrochloric acid (10 ml) and diethyl ether (10 ml) were added and the mixture stirred for 10 min. The organic layer was separated, washed with dilute hydrochloric acid (10 ml), and dried (Na_2SO_4). Distillation gave the alcohol in 78% yield.

Acknowledgement

We thank I.C.I. Fine Chemicals Manufacturing Organisation for financial support (to A.J.S.).

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